

## Synthesis of Mixed-metal Trinuclear Complexes. X-Ray Crystal Structure of $[(\text{cod})_2\text{Rh}_2(\mu_3\text{-C}_7\text{H}_4\text{NS}_2)_2\text{AgO}_2\text{ClO}_2]$ (cod = cyclo-octa-1,5-diene; $\text{C}_7\text{H}_4\text{NS}_2$ = benzothiazole-2-thiolate)

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The complex  $[(\text{Rh}(\mu_2\text{-C}_7\text{H}_4\text{NS}_2)(\text{cod}))_2]$  reacts with compounds of the group 11 metals to give heterotrinnuclear complexes, one of which, the title compound, has been characterized by X-ray diffraction methods showing short Rh–Ag separations in a bent arrangement.

There is considerable interest in the synthesis of heterometallic complexes because of their potential ability in processes requiring co-ordination of substrates to several metal centres.<sup>1</sup> Mixed-metal complexes or clusters containing gold atoms have become increasingly common but the related chemistry of silver is still poorly developed.<sup>2</sup> Although some of the recently reported mixed silver–rhodium compounds such as  $[\text{Rh}_3\text{Ag}_3\text{H}_9(\text{tripod})_3][\text{CF}_3\text{SO}_3]_3$  [tripod =  $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ ]<sup>3</sup> are formed serendipitously, isolobal relationships<sup>4</sup> and bridge-assisted addition reactions<sup>5</sup> are useful synthetic approaches. A related class of compounds now emerging concerns the aggregates<sup>6</sup> of co-ordinatively unsaturated complexes which have several metal atoms in close proximity but do not have metal–metal bonds, a characteristic feature of these metal clusters. The classification of these compounds in one or other category may be difficult if the metal–metal distances are near to those of the metal–metal bond. In this context, we describe here the preparation of the binuclear rhodium complex  $[(\text{Rh}(\mu_2\text{-C}_7\text{H}_4\text{NS}_2)(\text{cod}))_2]$  (**1**) (cod = cyclo-octa-1,5-diene,  $\text{C}_7\text{H}_4\text{NS}_2$  = benzothiazole-2-thiolate) which reacts through bridge-assisted addition reactions with compounds both of the group 11 metals and rhodium to give hetero- or homotrinnuclear aggregates. One of these has been structurally characterized showing a number of unusual features.

Reaction of  $[(\text{RhCl}(\text{cod}))_2]$  with lithium benzothiazole-2-thiolate in  $\text{Et}_2\text{O}$  gives the air-stable microcrystalline complex (**1**)<sup>†</sup> in 90% yield. Variable temperature <sup>1</sup>H n.m.r. studies provide evidence that complex (**1**) exists as a single isomer in the stopped exchange region at  $-60^\circ\text{C}$  and shows fluxional behaviour. Addition of silver perchlorate in acetone to a  $\text{CH}_2\text{Cl}_2$  solution of (**1**) at room temperature does not lead to

its oxidation. Instead the 'naked'  $\text{Ag}^+$  co-ordinates to the electron-rich sulphur atoms to form readily yellow crystals of the insoluble heterotrinnuclear complex  $[(\text{cod})_2\text{Rh}_2(\mu_3\text{-C}_7\text{H}_4\text{NS}_2)_2\text{AgO}_2\text{ClO}_2]$  (**2**) in 90% yield. The structure of the complex (**2**), depicted in Figure 1, has been fully elucidated by an X-ray diffraction study.<sup>‡</sup> It consists of two Rh and one Ag atoms in a bent arrangement with two molecules of benzothiazole-2-thiolate interacting with all three metals. Each ligand is bonded to one Rh atom through the nitrogen atom and asymmetrically bridges one Rh and one Ag atom through the sulphur. The Rh atoms complete their co-ordination with a cod ligand interacting through the two olefinic bonds, while the silver atom completes the co-ordination with two oxygen atoms from a perchlorate anion. The structure of (**2**) is comparable to that of the homotrinnuclear  $[\text{Rh}_3(\mu_3\text{-SC}_5\text{H}_4\text{N})_2(\text{CO})_6]^{+7}$  but in the latter the sulphur of the pyridine-2-thiolate ligand symmetrically bridges two Rh atoms and the Rh–Rh separations (*ca.* 2.90 Å) are much longer than the Rh–Ag ones in (**2**) [2.796(3) Å]. The Rh–Ag distances in (**2**) are shorter than those found in the  $[\text{Rh}_3\text{Ag}_3\text{H}_9(\text{tripod})_3]^{3+3}$  cation [in the range 2.795(4)–2.807(4) Å for the edges doubly bridged by hydrides and in the range 2.884(4)–2.933(4) Å for the edges with single hydride bridges] and longer than those found in the  $\text{Rh}_2\text{Ag}$  triangle of  $[\text{Rh}_2(\eta\text{-C}_5\text{H}_5)_2(\mu\text{-CO})(\mu\text{-dppm})(\mu\text{-AgOPF}_2\text{O})]$  [2.689(2) Å]<sup>8</sup> and correspond to the expected value for the Rh–Ag single bond (*ca.* 2.790 Å<sup>9</sup>).

Reaction of (**2**) with  $\text{PPh}_3$  in  $\text{CH}_2\text{Cl}_2$  gives an orange solution from which orange crystals of  $[(\text{cod})_2\text{Rh}_2(\mu_3\text{-C}_7\text{H}_4\text{NS}_2)_2\text{AgPPh}_3][\text{ClO}_4]$  (**3**) separate in 85% yield on addition of  $\text{Et}_2\text{O}$ . Complex (**3**) is a 1:1 electrolyte for which n.m.r. spectroscopic data evidence that the  $\text{PPh}_3$  group is bonded to silver and has a fluxional behaviour. Alternatively,

<sup>†</sup> Satisfactory elemental analyses and molecular weights were obtained for the new compounds described herein.

*Selected spectroscopic and physical data* (n.m.r. measured in  $\text{CDCl}_3$ ): (**1**) <sup>1</sup>H n.m.r. ( $-60^\circ\text{C}$ )  $\delta$  8.73 (d, 2H), 7.40 (dd of d, 2H), 7.13 (m, 4H) ( $\text{C}_7\text{H}_4\text{NS}_2$  ligands); 5.02 (m, 2H), 4.40 (m, 2H), 4.31 (m, 2H), 3.82 (m, 2H) (=C–H, cod); 2.8–2.3 (m, 8H), 2.1 (m, 8H) ( $>\text{CH}_2$ , cod).

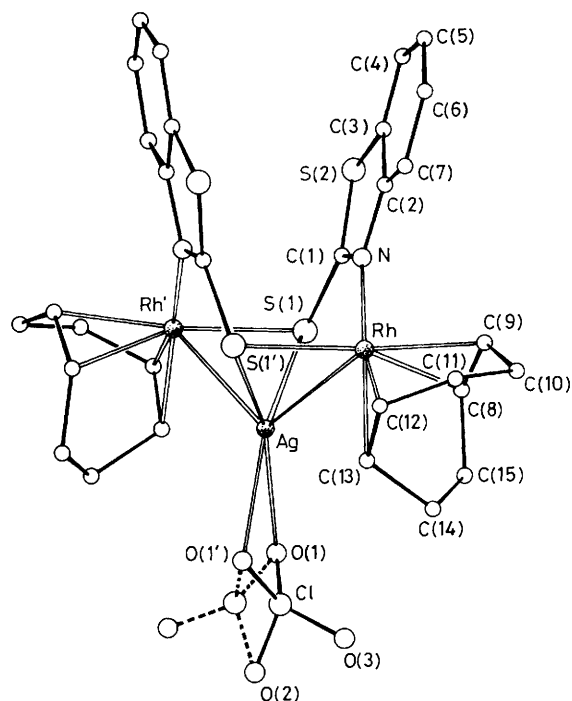
(**3**)  $\Lambda_c$  113  $\text{S cm}^2 \text{ mol}^{-1}$  (in  $5.6 \times 10^{-4} \text{ mol dm}^{-3}$  acetone solution). <sup>31</sup>P{H} n.m.r. ( $-40^\circ\text{C}$ )  $\delta$  15.8 [two d,  $1J(^{109}\text{Ag}^{31}\text{P})$  660,  $1J(^{107}\text{Ag}^{31}\text{P})$  572 Hz].

(**4**) <sup>1</sup>H n.m.r. ( $-20^\circ\text{C}$ )  $\delta$  8.64 (d, 2H), 7.40 (t, 2H), 7.03 (t, 2H), 6.97 (d, 2H) ( $\text{C}_7\text{H}_4\text{NS}_2$  ligands); 5.10 (m, 2H), 4.62 (m, 2H), 4.35 (m, 2H), 3.56 (m, 2H) (=C–H, cod); 3.3 (m, 2H), 3.0 (m, 2H), 2.7–2.4 (m, 4H), 2.3–1.9 (m, 4H), 1.8–1.6 (m, 4H) ( $>\text{CH}_2$ , cod).

(**5**)  $\Lambda_c$  130  $\text{S cm}^2 \text{ mol}^{-1}$  (in  $5.0 \times 10^{-4} \text{ mol dm}^{-3}$  acetone solution). <sup>1</sup>H n.m.r. ( $20^\circ\text{C}$ )  $\delta$  8.49 (d, 2H), 7.32 (t, 2H), 7.05 (d, 2H), 6.92 (t, 2H) ( $\text{C}_7\text{H}_4\text{NS}_2$  ligands); 5.67 (m, 2H), 5.46 (m, 2H), 4.70 (m, 2H), 4.30 (m, 2H), 3.7 (m, 4H) (=C–H, cod); 3.4–2.9 (m, 6H), 2.7–2.0 (m, 12H), 1.9–1.5 (m, 6H) ( $>\text{CH}_2$ , cod).

<sup>‡</sup> *Crystal data for (2)*:  $\text{C}_{30}\text{H}_{32}\text{AgClN}_2\text{O}_4\text{Rh}_2\text{S}_4$ ,  $M = 961.97$ , orthorhombic, space group  $Pbcn$ ,  $a = 7.635(5)$ ,  $b = 27.564(11)$ ,  $c = 15.564(8)$  Å,  $U = 3275(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.951$  g  $\text{cm}^{-3}$ ,  $F(000) = 1904$ ,  $\lambda = 0.71069$  Å,  $\mu(\text{Mo-K}\alpha) = 19.34$   $\text{cm}^{-1}$ . The intensities of 3586 independent reflections were collected on a Siemens AED diffractometer (with  $\theta$  in the range  $3\text{--}27^\circ$ ) using the  $\theta/2\theta$  scan technique and the niobium-filtered Mo-K $\alpha$  radiation. The structure was solved by direct and Fourier methods and refined by full-matrix least-squares on the basis of 1863 observed reflections [ $I \geq 2\sigma(I)$ ] with anisotropic thermal parameters for the non-hydrogen atoms except those of the perchlorate anion. This was found disordered and distributed in two positions of equal occupancy factor with three oxygen atoms in common (see Figure 1). All hydrogen atoms were placed in their geometrically calculated positions and introduced in the final structure factor calculations. Final  $R$  and  $R_w$  values 0.062 and 0.079.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.



**Figure 1.** View of the structure of the complex  $[(\text{cod})_2\text{Rh}_2(\mu_3\text{-C}_7\text{H}_4\text{NS}_2)_2\text{AgO}_2\text{ClO}_2]$  (2) with the atomic numbering scheme. Important bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ): Ag–Rh 2.796(3), Ag–S(1) 2.609(3), Ag–O(1) 2.53(2), Rh–S(1') 2.358(3), Rh–N 2.080(9), Rh–C(8) 2.108(14), Rh–C(9) 2.131(15), Rh–C(12) 2.131(15), Rh–C(13) 2.166(14); Rh–Ag–Rh' 110.5(1), S(1)–Ag–Rh 85.4(1), S(1')–Ag–Rh 51.6(1), Ag–Rh–S(1') 60.1(1), Ag–Rh–N 90.1(3), S(1')–Rh–N 93.7(3), Ag–S(1)–Rh' 68.3(1). The primed atoms are related to the unprimed ones by a two-fold axis.

complex (3) is obtained by reaction of (1) with  $[\text{Ag}(\text{ClO}_4)\text{PPh}_3]$  in  $\text{CH}_2\text{Cl}_2$ .

From Figure 1 it is likely that the silver cation enters in the preformed site determined by the sulphur atoms in the structure of (1). To test this hypothesis complex (1) was reacted with  $\text{CuCl}$  in  $\text{CH}_2\text{Cl}_2$  giving an orange solution of

$[(\text{cod})_2\text{Rh}_2(\mu_3\text{-C}_7\text{H}_4\text{NS}_2)_2\text{CuCl}]$  (4) which is isolated as yellow-orange crystals from  $\text{CH}_2\text{Cl}_2\text{-Et}_2\text{O}$ . Complex (1) reacts also with the species  $[\text{Rh}(\text{cod})(\text{Me}_2\text{CO})_2]^+$  in acetone to give a dichroic green-red solution from which the dark-green complex  $[\text{Rh}_3(\mu_3\text{-C}_7\text{H}_4\text{NS}_2)_2(\text{cod})_3][\text{ClO}_4]$  (5) is obtained on addition of  $\text{Et}_2\text{O}$ . The dark colour and dichroism in solution is indicative of short metal-metal distances.  $^1\text{H}$  N.m.r. spectra of (4) and (5) are consistent with a structure similar to that of complex (2) in which the 'CuCl' or 'Rh(cod)' moieties occupy the position of the 'AgO<sub>2</sub>ClO<sub>2</sub>' group. In a similar way  $[\text{AuCl}(\text{tht})]$  (tht = tetrahydrothiophene) reacts with (1) in  $\text{CH}_2\text{Cl}_2$  to give  $[(\text{cod})_2\text{Rh}_2(\mu\text{-C}_7\text{H}_4\text{NS}_2)_2\text{AuCl}]$  (6) in 65% isolated yield.

We thank the C.A.I.C.Y.T. (Spain) for financial support.

Received, 21st July 1986; Com. 1020

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